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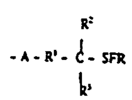
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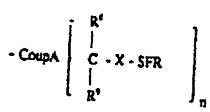
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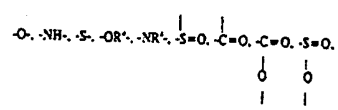
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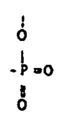
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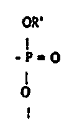
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(57) Abstract

A modified particle is disclosed wherein a particle has an attached group having formula (I), wherein A represents an aromatic group or an alkyl group; R^1 represents a bond, an arylene group, an alkylene group (i), (ii) or (iii), wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein R^5, which is the same or different, represents an alkyl group or an aryl group; and SFR represents a stable free radical. Also disclosed is a modified particle or aggregate having attached a group having formula (II), wherein CoupA represents an Si-containing group, a Ti-containing group, a Cr-containing group or a Zr-containing group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NHR^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein R^{10} represents an alkyl group or an aryl group; SFR represents a stable free radical; and n is an integer of from 1 to 3. A modified particle having an attached –SFR or –X–SFR is additionally disclosed. Also, modified particles with attached polymers are also disclosed as well as methods of making the modified particles.

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PARTICLES HAVING AN ATTACHED STABLE FREE RADICAL, POLYMERIZED MODIFIED PARTICLES, AND METHODS OF MAKING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to particles, such as carbon black, having an attached stable free radical which permits the formation of modified particles having blocked radical sources. The present invention further relates to methods of preparing and using such modified particles.

The role of carbon black as a thermal stabilizer in polymeric systems is discussed by W. L. Hawkins, R. H. Hansen, W. Matreyek, F. H. Winslow; *J. Applied Polymer Science*, vol. 1, pages 37-42, 1959; J. T. Cruver, K. W. Rollmann: *J. Applied Polymer Science*, vol. 8, pages 1169-83, 1964, and by G. Ivan, M. Giurgina: *Revue Roumaine de Chemie*, vol. 29, number 8, pages 639-646, 1984. In each discussion the mechanism is through phenolic and quinone oxygen groups on the carbon black surface behaving either as radical traps or peroxide decomposers. One skilled in the art, however, would consider these sites unavailable as initiating sites for polymerization processes.

Belmont et al. (J. A. Belmont, J. M. Funt: International Rubber Conference, Essen, Germany, June 24-27 1991) identified the presence of peroxide groups, typically in the range of 0.1 to 0.4 micromoles/sq meter, on the carbon black surface. However, the majority (greater than 80%) of the peroxide groups are thermally stable to heat treatment at 200 °C and hence cannot be considered to be potential initiating sites for radical polymerization.

Tsubokawa et al. (K. Fujiki, N. Tsubokawa, Y. Sone: *Polymer J.*, vol. 22, number 8, pages 661-70, 1990, and N. Tsubokawa: *Prog. Polymer Science*, vol. 17, pages 417-70, 1992) discuss growing polymers from an activated carbon black surface by first attaching a reactive group via the oxygen groups on the carbon black surface. Typical examples include the use of glycidyl methacrylate where the glycidyl group reacts with phenolic hydroxyl groups on the carbon black surface providing a vinyl functionality; the reaction of 4,4' azo bis-(4-cyanovaleric acid) whereby the isocyanate group reacts with phenolic hydroxyl groups and

subsequent heating decomposes the azo group to generate an alkyl radical; and the reaction of the phenolic hydroxyl groups with butyl lithium which can then be used as an initiation site for anionic polymerization.

All of these approaches require the presence of oxygen groups on the carbon black surface. Since the level of reactive hydroxyl and carboxylic acid groups, relative to the above approaches, present on a typical furnace or thermal carbon black is typically 0.01 to 0.1 micromoles/sq meter, the number of potential initiation sites is quite low.

Further, subsequent polymerization from these activated sites will most likely occur in the normal manner for free radical polymerization with the chains being irreversible terminated by chain combination reactions, combination with unreacted oxygen groups on the carbon black surface, and/or the addition of chain stoppers. In all cases the polymerization cannot be reinitiated. Accordingly, there is a need to provide particles with attached stable free radicals which overcome the above-described limitations.

SUMMARY OF THE INVENTION

In accordance with the purposes of the present invention, the present invention relates to a modified particle which includes a particle having an attached group having the formula:

$$-A-R^1-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{C}}-SFR \qquad \text{(I)},$$

wherein A represents an aromatic group or an alkyl group; R^1 represents a bond, an arylene group, an alkylene group,

$$\text{-O-, -NH-, -S-, -OR}^4\text{-, -NR}^4\text{-, } -\overset{|}{S}=O,\ -\overset{|}{C}=O,\ -\underset{\underset{|}{\underset{O}{|}}}{C}=O,\ -\underset{\underset{|}{\underset{O}{|}}}{S}=O,$$

$$\begin{array}{c} | \\ O \\ | \\ -P=O \\ \| \\ O \end{array} \quad \text{or,} \quad \begin{array}{c} OR^4 \\ | \\ -P=O \\ | \\ O \\ | \end{array}$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$ or $-SR^5$, wherein R^5, which can be the same or different, represents hydrogen, an alkyl group or an aryl group; and SFR represents a stable free radical.

The present invention further relates to a modified particle or aggregate wherein the particle or aggregate is a carbon-metal multiphase aggregate, a carbon-silicon containing species multiphase aggregate, a metal oxide, or a metal hydroxide. Attached to the particle or aggregate is a group having the formula:

$$-\mathrm{CoupA}\left[\begin{array}{c} R^8 \\ | \\ C - \mathrm{SFR} \\ | \\ R^9 \end{array}\right]_n \qquad \text{(II)},$$

wherein CoupA represents a Si-containing group, a Ti-containing group, a Cr-containing group, or a Zr-containing group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NHR^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein R^{10}, which can be the same or different, represents hydrogen, an alkyl group or an aryl group; SFR represents a stable free radical, and n is an integer of from 1 to 3.

The present invention further relates to a modified particle with an

attached polymer or blocked radical sources, wherein the modified particle has an attached group having the formula:

$$-A-R^1-\underset{\displaystyle R^3}{\underset{|}{\overset{\displaystyle R^2}{\overset{|}{C}}}}-X-SFR \qquad \text{(III)},$$

wherein X represents blocked radical sources or a polymer formed from at least one polymerizable vinyl or diene based monomer, A represents an aromatic group or alkyl group; R^1 represents a bond, an arylene group, an alkylene group,

$$-O-,\ -NH-,\ -S-,\ -OR^4-,\ -NR^4-,\ \overset{|}{-S}=O,\ \overset{|}{-C}=O,\ -\underset{\underset{|}{O}}{\underset{|}{C}}=O,\ -\underset{\underset{|}{O}}{\underset{|}{S}}=O,$$

$$\underset{\underset{\displaystyle O}{\|}}{-\overset{\overset{|}{O}}{\overset{|}{P}}=O} \quad \text{or,} \quad \underset{\underset{|}{O}}{\underset{|}{-\overset{\overset{\displaystyle OR^4}{|}}{P}}}=O$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$ or $-SR^5$, wherein R^5, which can be the same or different, represents an alkyl group or an aryl group; and SFR represents a stable free radical.

The present invention also relates to another modified particle having an attached polymer. The particle is a carbon-metal multiphase aggregate, a carbon-silicon containing species multiphase aggregate, a metal oxide, or a

metal hydroxide. Attached to the particle is a group having the formula:

$$- \mathrm{CoupA} \left[\begin{array}{c} R^8 \\ | \\ C - X - \mathrm{SFR} \\ | \\ R^9 \end{array} \right]_n \qquad \text{(IV)},$$

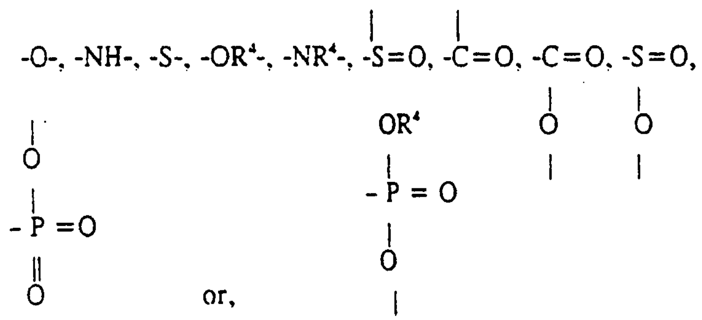
wherein CoupA represents a Si-containing group, a Ti-containing group, a Cr-containing group, or a Zr-containing group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NHR^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein R^{10}, which can be the same or different, represents an alkyl group or an aryl group; SFR represents a stable free radical, X is blocked radical sources or a polymer formed from at least one polymerizable vinyl or diene containing monomer, and n is an integer of from 1 to 3.

The present invention, in addition, relates to a method for preparing and using these various modified particles. The method includes reacting a particle having an attached vinyl substituted alkyl group with a reactive free radical source and a stable free radical source to form a reaction product. The present application further relates to forming the modified particles with an attached blocked radical source or polymer by reacting the reaction product with a polymerizable vinyl or diene containing monomer.

The present invention further relates to a method of making a modified particle comprising a particle having attached a group having the formula:

$$- A - R^1 - \begin{array}{c} R^2 \\ | \\ C \\ | \\ R^3 \end{array} - \mathrm{SFR} \qquad \text{(I)},$$

wherein A represents an aromatic group or an alkyl group; R^1 represents a bond, an arylene group, an alkylene group,



wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein R^5, which is the same or different, represents an alkyl group or an aryl group; and SFR represents a stable free radical, wherein said method comprises reacting a) a particle having attached an aromatic group or an alkyl group with a group containing an abstractable proton and which leaves behind a carbon-centered radical when the proton is abstracted with b) a reactive free radical source and c) a stable free radical source.

The present invention, in addition, relates to a modified particle which includes a particle having an organic group having a - SFR group, where the organic group is directly attached to the particle. The modified particle can also be a particle having an organic group having an -X-SFR group, where the organic group is directly attached to the particle.

The present invention further relates to polymer-modified particles or aggregates where the –SFR group is replaced or terminated with a terminated moiety, for example, a hydrogen atom, a hydroxy group, or a halide group.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

In one embodiment, the present invention relates to a modified particle comprising a particle having attached a group having the formula:

$$\begin{array}{c} R^2 \\ | \\ -A-R^1-C-SFR \\ | \\ R^3 \end{array} \qquad (I),$$

wherein A represents an aromatic group or an alkyl group which is attached to the particle; R^1 represents a bond, an arylene group, an alkylene group,

$$-O-,\ -NH-,\ -S-,\ -OR^4-,\ -NR^4-,\ \begin{array}{c} | \\ -S=O \end{array},\ \begin{array}{c} | \\ -C=O \end{array},\ \begin{array}{c} -C=O \\ | \\ O \\ | \end{array},\ \begin{array}{c} -S=O \\ | \\ O \\ | \end{array},$$

$$\begin{array}{c} | \\ O \\ | \\ -P=O \\ \| \\ O \end{array} \quad \text{or,} \quad \begin{array}{c} OR^4 \\ | \\ -P=O \\ | \\ O \\ | \end{array}$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein R^5, which can be the same or different, represents an alkyl group or an aryl group; and SFR represents a stable free radical.

The particle, to be modified, can be any particle capable of having a

group represented by any one of formulas described herein attached thereto, such as formula (I)-(IV). Preferably, the particle has a carbon reactive site (C-), since in a preferred embodiment for the groups of formula (I) and (III), -SFR and -X-SFR are preferably attached through a carbon bond on the particle. The particle, for instance, can be carbon products, colored pigments other than carbon products, metal oxides (e.g., silica), metal hydroxides, multiphase aggregates comprising a carbon phase and a silicon-containing species phase, multiphase aggregates comprising a carbon phase and a metal-containing species phase, and the like. The carbon may be of the crystalline and/or amorphous type. Examples of carbon products include, but are not limited to, graphite, carbon black, vitreous carbon, activated charcoal, activated carbon, carbon fiber, and mixtures thereof. Finely divided forms of the above are preferred. Most preferably, the particle is a carbon product, and most preferably carbon black.

The multiphase aggregate containing the carbon phase and the silicon-containing species phase can also be considered a silicon-treated carbon black aggregate and the multiphase aggregate containing a carbon phase and a metal-containing species phase can be considered to be a metal-treated carbon black aggregate as long as one realizes that in either case, the silicon-containing species and/or metal-containing species are a phase of the aggregate just like the carbon phase. The multiphase aggregates do not represent a mixture of discrete carbon black aggregates and discrete silica or metal aggregates and is not a silica coated carbon black. Rather, the multiphase aggregates used in the present invention include at least one silicon-containing or metal-containing

region concentrated at or near the surface of the aggregate (but put of the aggregate) and/or within the aggregate.

The aggregate, thus contains at least two phases, one of which is carbon and the other of which is a silicon-containing species, a metal-containing species, or both. The silicon-containing species that can be a part of the aggregate is not attached to a carbon black aggregate like a silica coupling agent, but actually is part of the same aggregate as the carbon phase. For instance, when the multiphase aggregate having a carbon phase and a silicon-containing species phase is examined under STEM-EDX, the silicon signal corresponding to the silicon-containing species is found to be present in individual carbon black aggregates. By comparison, for example, in a physical mixture of silica and carbon black, STEM-EDX examination reveals distinctly separate silica and carbon black aggregates.

The metal-treated carbon blacks are aggregates containing at least one carbon phase and at least one metal-containing species phase. The metal-containing species include compounds containing aluminum, zinc, magnesium, calcium, titanium, vandium, cobalt, nickel, zirconium, tin, antimony, chromium, neodymium, lead, tellurium, barium, cesium, iron, and molybdenum. Preferably, the metal-containing species phase is an aluminum- or zinc-containing species phase. The metal-containing species phase(s) can be distributed through at least a portion of the aggregate and is an intrinsic part of the aggregate.

Further, it is within the bounds of the present invention to have a metal-treated carbon black containing more than one type of metal-containing species

phase or the metal-treated carbon black can also contain a silicon-containing species phase and/or a boron-containing species phase. For example, the metal-treated carbon black of the present invention can have an aggregate comprising a carbon phase, an aluminum-containing species phase, and a zinc-containing species phase. Accordingly, the multiphase aggregates used in the present invention can have two or more different types of metal-containing species phases and/or additional non-metal species phases.

Preferably, for purposes of the present invention, the amount of elemental silicon and/or elemental metal present in the multiphase aggregate is from about 0.1 to about 25 wt. %, more preferably, from about 0.5 wt. % to about 10 wt. %, and most preferably from about 0.2 wt. % to about 5.4 wt. %, by weight of the aggregate.

The details of making the multiphase aggregates are explained in U.S. Patent Appl. Nos.: 08/446,141, filed May 22, 1995; 08/446,142, filed May 22, 1995; 08/528,895, filed September 15, 1995; and 08/750,017, filed November 22, 1996, which is a National Phase Application of PCT No. WO 96/37547, filed May 21, 1996, U.S. Patent Appl. No. 08/828,785, filed March 27, 1997, U.S. Patent Appl. Nos. 08/837,493 filed April 18, 1997 and 09/061,871 filed April 7, 1998. All of these patent applications are hereby incorporated in their entireties herein by reference.

A silica-coated carbon product can also be used as the particle, such as that described in PCT Application No. WO 96/37547, published November 28, 1996, which is hereby incorporated in its entirety herein by reference.

The colored pigment is any pigment which can be modified with the

attachment of an aromatic group or an alkyl group. The colored pigments other than carbon products include, but are not limited to, black, blue, brown, cyan, green, violet, magenta, red, yellow, as well as mixtures thereof. Suitable classes of colored pigments include, but are not limited to, anthraquinones, phthalocyanine blues, phthalocyanine greens, diazos, monoazos, pyranthrones, perylenes, heterocyclic yellows, quinacridones, and (thio)indigoids. Specific examples and further information concerning the colored pigments and methods of making colored pigments with attached aromatic groups or alkyl groups are described in PCT Publication No. WO 97/47699, incorporated in its entirety by reference herein.

Particles useful for the present invention may, for example, have primary particles sizes in the general range of from about 10 nm to about 500 nm, and preferably from about 10 nm to about 250 nm, and primary aggregate sizes in the general range of from about 50 nm to about 100 microns, preferably from about 50 nm to about 10 microns, still more preferably from about 75 nm to about 1 micron. The BET surface area of these particles can be any suitable surface area and preferably ranges from about 10 m^2/g to about 2000 m^2/g and more preferably, from about 10 m^2/g to about 1,000 m^2/g, and still more preferably from about 50 m^2/g to about 500 m^2/g; and the particle structure preferably ranges from about 10 cc/100g to about 1000 cc/g, more preferably, from about 50 cc/100g to about 200cc/100g.

The number of SFR groups directly attached to the particle prior to polymerization can be any amount which can be effectively attached. For instance, the number of -SFR groups may range from about 0.01 mmole/g (of

particle) to about 10 mmole/g, or from about 0.1 mmole/g to about 4 mmole/g, or from about 0.05 mmole/g to 4 mmole/g or from about 0.5 mmole/g to about 3 mmole/g, or from about 0.1 mmol/g to about 2 mmol/g.

When the particle is a multiphase aggregate, like a particle comprising a carbon phase and a silicon-containing species phase, preferably the group of formula (I) or (III) is attached at least, if not exclusively, on the carbon phase.

With regard to the A group, which represents at least one aromatic group or an alkyl group, any aromatic group or alkyl group may be used. Unlike the polymerizable monomer discussed later, the aromatic group or the alkyl group is not a polymer and is not polymerized. Examples include, but are not limited to, arylene groups. Preferred arylene groups include, but are not limited to, phenylene and naphthalene groups. The aromatic group includes, but is not limited to, unsaturated cyclic hydrocarbons containing one or more rings. The aromatic group may be substituted or unsubstituted. Aromatic groups include aryl groups (for example, phenyl, naphthyl, anthracenyl, and the like), and heteroaryl groups (for example, imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl, triazinyl, indolyl, and the like). The alkyl group is preferably a C_1-C_{12} alkyl group, and may be branched or unbranched, and is preferably ethyl.

With respect to R^1, preferred arylene groups include, but are not limited to, benzene ring containing groups. Preferred alkylene groups include, but are not limited to, C_1 - C_{18} alkylene-containing groups. These groups can be linear, branched, or unsaturated. These examples of arylene and alkylene groups can also be considered examples of R^4. Preferred alkyl groups for R^4

are C_1-C_{20} alkyl groups, more preferably C_1-C_5 alkyl groups and preferred aryl groups are phenyl, biphenyl, and naphthyl.

With respect to R^2 and R^3, which can be the same or different, examples of alkyl groups (e.g. C_1-C_{20} alkyl group) include, but are not limited to, methyl, ethyl, propyl, butyl, and the like. Preferably, the alkyl group is a C_1-C_5 alkyl group. Examples of aryl groups include, but are not limited to, phenyl, biphenyl, and naphthyl. The alkyl and aryl groups mentioned here as well as the arylene and alkylene groups mentioned throughout can be unsubstituted or substituted for purposes of the present invention. R^5 can be the same type of alkyl and aryl groups mentioned above with respect to R^2 and R^3.

SFR, which is the stable free radical, can be any radical capable of capping the remaining portion of the group attached onto the particle. Examples of the SFR include, but are not limited to, nitroxide free radicals such as 2,2,5,5-tetramethyl-pyrrolidinyloxy and 2,2,6,6-tetramethyl-piperindinyloxy, organic hydrazyl compounds, organic verdazyl compounds, organic aroxyl compounds (e.g., 2,4,6 tri-tertiary butyl phenoxy radical, galvinoxyl (2,6 ditertiary butyl alpha 3,5 ditertiary butyl oxo 2,5 cyclohexadiene-1 ylidene para tolyoxy) radical), aryl alkyl or aryl cycloalkyl where the unpaired electron is on a carbon atom, substituted triphenyl methyl, substituted triphenyl amine, and derivatives of these compounds.

The SFR used in the present invention preferably has the formulas:

$$-O-N\begin{matrix} \diagup R^6 \\ \\ \diagdown R^7 \end{matrix} \qquad (V) \qquad \text{or}$$

$$- O - Ar^2 \qquad \text{(VI)}$$

wherein R^6 and R^7, which can be the same or different, each represent a substituted or unsubstituted alkyl or cycloalkyl group; or R^6 and R^7 can together form a cycloalkyl group; Ar^2 represents a substituted or unsubstituted aromatic group. Representative examples of the alkyl and aromatic groups can be the same as described above with respect to the substitutents R^2 and R^3.

Another embodiment of the present invention relates to a modified particle or aggregate having a group of formula (II) attached thereto. The particle can be a metal oxide, a metal hydroxide, an aggregate comprising at least one carbon phase and at least one metal-containing species phase, or an aggregate comprising at least one carbon phase and at least one silicon-containing species phase. Attached to this particle or aggregate is a group having the formula:

$$- \text{CoupA} \left[\begin{array}{c} R^8 \\ | \\ C \ \text{- SFR} \\ | \\ R^9 \end{array} \right]_n \qquad \text{(II)},$$

wherein CoupA represents a Si-containing group, a Ti-containing group, a Cr-containing group; or a Zr-containing group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NHR^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein each R^{10} , which can be the same or different, represents an alkyl group or an aryl group; SFR represents a stable free radical,

and where n is an integer of from 1 to 3. Preferably, CoupA is attached to the particle or aggregate, especially in the case of a Si-containing group, via an oxygen radical which can form a part of a CoupA.

Examples of Si-containing groups include, but are not limited to, dimethylsilylmethyl, dialkoxysilylmethyl, and the like. Examples of Ti-containing groups include, but are not limited to, alpha substituted tri-acetyl titanate and the like. Examples of Zr-containing groups include, but are not limited to, dialpha methoxy neopentylzirconate, aluminum zirconates, and the like.

Examples of the substituents R^8 and R^9 can be the same as the substituents R^2 and R^3 mentioned above. Likewise, examples of the substituent R^{10} can be the same as the substituent R^5 discussed above. Also, the SFR is the same as discussed above.

The modified particles having the attached group of the formulas, such as formula (I), can be made in the following manner. A particle, such as carbon black, can first have a vinyl substituted aromatic group or a vinyl substituted alkyl group attached to the particle. This attachment can be accomplished by the methods described in PCT International Application No. WO 96/18688 and U.S. Patent Nos. 5,630,868; 5,559,169; 5,571,311; and 5,559,169 as well as U.S. Patent Application No. 08/572,525, all of which are hereby incorporated in their entireties by reference herein.

The particle having the attached vinyl substituted aromatic group or the vinyl substituted alkyl group is then reacted with a reactive free radical source and a stable free radical source for a sufficient time and at a sufficient

temperature to form the modified particle having the attached group, like that of formula (I). The molar ratio of the reactive free radical source to the stable free radical source is from about 0.7 to about 2.0, and preferably from about 0.9 to about 1.1. Examples of the reactive free radical source include, but are not limited to, radicals generated from organic peroxides such as benzoyl peroxides and azo initiators such as azobisisobutyronitrile, and the like. The reactive free radical source is present in amounts sufficient to react with the vinyl aromatic group or vinyl alkyl group present on the particle. Preferably, the amount of the reactive radical source is from about 0.01 mmoles/g (of particle) to about 10 mmoles/g and more preferably from about 0.01 to about 5 mmoles/g.

Alternatively, the modified particles of the present invention can be made by first forming the groups of the formulas described above, such as formula (I). Preferably, the stable free radical group is attached in the meta or para position of the aromatic group, if one is used. The group having the aromatic group or alkyl group with the stable free radical group is then attached to the particle by a diazonium treatment in the manner described in the above referenced patents and patent applications, where a diazonium salt will first be formed containing a group of one of the formulas described above in the manner described in the above-referenced patents. The groups of the formulas can be then subsequently attached to the particle. In a less preferred way, the formulas of the present invention can be attached to the particle through a hydroxyl or carbonyl group present on the particle. Also, the modified particle of the present invention can be formed by attaching a stable

free radical compound containing at least one alkoxy silyl, alkoxy titanyl, or alkoxy zirconyl group to the particle which, in this particular process is preferably a metal oxide or metal hydroxide, or a carbon surface. This particular embodiment would attach a group of formula (II) or (IV) to a particle.

In another process, the modified particle can be formed by first taking an aromatic group or an alkyl group and reacting it with a compound to form the groups of the formulas described above except for the presence of the -SFR group. In other words, a group having the formula $A\text{-}R^1\text{-}CR^2R^3$ would first be formed and then the -SFR would be attached to this group to form a group of formula (I) of the present invention which can then be attached to the particle. In this process, R^2 and R^3 are preferably hydrogen.

A related process involves first taking an aromatic group or an alkyl group, such as a group having the formula $A\text{-}R^1\text{-}CR^2R^3$ and attaching it onto the particle, for instance by a diazonium treatment in a manner described above, and then attaching the -SFR group to form a group of formula (I) of the present invention. Example 7 of the present application shows a specific embodiment of this process. In more detail, this process involves proton abstraction wherein a group containing an abstractable proton which leaves behind a carbon-centered radical is attached onto an aromatic group or an alkyl group, wherein the aromatic group or the alkyl group is directly attached to the particle. For purposes of this process, the aromatic group or the alkyl group can first be attached to the particle and then subsequently a group containing the abstractable proton can then be attached or an aromatic group or an alkyl group

containing an abstractable proton can be attached onto the particle, for instance, by a diazonium treatment as described above. Then, a reactive free radical source and a stable free radical source are reacted with the particle having the attached aromatic group or alkyl group with the group containing an abstractable proton for a sufficient time and at a sufficient temperature to form the modified particle having the attached group, like that of formula (I). This modified particle having the attached group, like that of formula (I) can then be subjected to polymerization reactions in order to have polymers attached thereto such as set forth in formula (III). In this process, the reactive free radical source abstracts the proton from the group containing the abstractable proton which thus leaves a carbon-centered radical behind which permits the stable free radical source to attached thereto to create the modified particles of the present invention such as set forth in formula (I). Examples of a group containing an abstractable proton which leaves behind a carbon-centered radical include alkyl groups, alkenes with a hydrogen atom in the alpha position to the olefinic bond, and the like. Specific examples include C_1-C_{20} alkyl groups, such as methyl, ethyl, propyl, butyl, and the like. The reactive free radical source for this process can be organic peroxides such as benzoyl peroxides and t-butyl peroxides. Examples of the stable free radical source are described above and can be the same for this process. This process can also be applied where the modified particle aggregate has a group attached like that of formula (II) and (IV).

Alternatively, the process of making the modified particles of the present invention can be a three step process where the alkyl or aromatic group

is first attached to the particle and then the group having the formula R^1-C-R^2R^3 can be attached to the aromatic group or alkyl group. Then in a third step, the -SFR can be attached to the R^1-C-R^2R^3 group.

Also, in making the modified particles having the attached group of one the formulas described above, an aliphatic vinyl group can be attached to the particle surface by a diazotisation of a vinyl substituted amino aromatic or alkyl compound, or a vinyl substituted alkoxy silyl, titanyl, or zirconyl derivative. The vinyl group is then reacted with an organic peroxide and a stable free radical such that the organic peroxide and stable free radical are present in an amount sufficient to react with at least one percent of the vinyl groups and preferably from about 50 to about 100% of the vinyl groups and the mole ratios of the organic peroxide to stable free radical are preferably from about 0.5:1 to about 1:1.

The modified particles of formula (II) can be made in the following manner. The aggregate comprising at least one carbon phase and at least one metal-containing species phase can be made as described in U.S. Patent Application No. 08/828,725, hereby incorporated herein by reference. The aggregate comprising at least one carbon phase and at least one metal containing species phase can be made as described in U.S. Patent Application No. 08/446,141 and 08/750,017. The aggregate or particle can then be reacted with a coupling agent by adding the coupling agent to the aggregate in a medium and mixing. Then, the aggregate or particle having the attached coupling group can be reacted with a reactive radical source and stable free radical source as described above.

For purposes of the above-described reactions, the reaction should occur for a time and temperature sufficient to form the attached group onto the particle or aggregate. Generally, this time is from about 3 minutes to about 96 hours and more preferably from about 1 hour to about 24 hours. The temperature of the reaction is dependent on the half-life of the peroxide, preferably from about 50°C to about 200°C, and more preferably from about 75°C to about 125°C.

For the various methods described above, any solvent, aqueous or non-aqueous, can be used. Preferably, the solvent does not interfere with the radical on the particle. Preferably, the solvent is toluene, benzene, or xylene. Mixtures of various solvents can be used as well.

With the modified particles described above, polymers can be attached onto these attached groups by reacting these modified particles or aggregates with one or more polymerizable monomer(s) such as a vinyl or diene containing monomer. Specific examples of such monomers include, but are not limited to styrene, isoprene, butadiene, chloromethylstyrene, methyl methacrylate, and butyl methacrylate, as well as acrylic acid and esters of acrylic acid and methacrylic acid and esters of methacrylic acid. More specific monomer examples include, but are not limited to, hydroxyalkyl (meth)acrylates, such as hydroxyethyl (meth)acrylate, hydroxyproyl (meth)acrylate; alkyl (meth)acrylates such as methyl acrylate or butyl acrylate; glycidyl (meth)acrylate; dimethylaminoethylacrylate; 2-acryl trimethyl ethylammonium chloride; aminoethyl acrylate; acrylonitrile; vinyl acetate, and the like. Mixtures of two or more monomers can be also used and/or polymerized

sequentially. For purposes of the present invention, the vinyl containing monomer includes vinyl containing monomers having additional olefinic groups which are conjugated or unconjugated to the vinyl containing monomer.

The polymerization reaction is conducted under conditions which permits the polymerization of the monomer so that it forms a part of the group attached onto the particle or aggregate. These conditions are preferably heating modified particles with a monomer above 80°C, preferably from about 120°C to about 150°C, optionally in the presence of a solvent. The reaction can be ended by lowering the temperature below 80°C. The polymer-modified particle can then be subjected to distillation, steam stripping, or precipitation or other known methods in order to remove residual monomers and solvents.

The polymerization reaction thus can produce any length of polymer on the modified particle or aggregate. For example, polymers having average molecular weights, preferably ranging from about 500 to about 1,000,000 can be made. Other ranges of average molecular weights include, but are not limited to, from about 500 to about 3,000, and from about 500 to about 2,000, and from about 500 to about 500,000, and from about 1,000 to about 250,000. The polymers can be any type, such as homopolymers, co-polymers, ter-polymers, or higher chain polymers. The polymers can also be block, graft, or random-type polymers. The polymers can be branched or unbranched. Polymers, such as comb polymers, can be formed or located off of the main polymer chain, and these polymers can be any type of polymer. Specific examples include, but are limited to, polyamines, such as polyethyleneimine or polyalkylene oxides, grafted onto the main polymer chain. The polymers that

are formed can be ionic (e.g., cationic or anionic) or non-ionic polymers. Specific examples of polymers include, but are limited to, polyamides, polyacrylics, polyvinylacetates, polyvinylalcohols, polyvinylpyridines, polyvinylpyrrilodones, polyvinylimidazoles, and acrylamides and derivatives thereof as well as combinations thereof.

Once the polymerization occurs, the modified particle will have a group attached having the formula:

$$-A-R^1-\underset{\displaystyle R^3}{\overset{\displaystyle R^2}{\overset{|}{\underset{|}{C}}}}-X-SFR \qquad \text{(III)},$$

wherein the substituents are the same as described earlier for formula (I) and X represents a polymer formed from at least one polymerizable vinyl or diene containing monomer.

Similarly, when the modified particle or aggregate having a group of formula (II) is polymerized by the introduction of one or more monomers, the group attached to the particle or aggregate will have the formula:

$$-\text{CoupA}\left[\begin{array}{c} R^8 \\ | \\ C \\ | \\ R^9 \end{array} \!\!\begin{array}{c} \\ \\ -X-SFR \\ \\ \\ \end{array}\right]_n \qquad \text{(IV)},$$

wherein the substituents are the same as described in formula (II) and X represents a polymer formed from at least one polymerizable vinyl or diene

containing monomer.

In another embodiment, a modified particle has an organic group containing a -SFR group directly attached to the particle. Preferably, the -SFR group is directly attached to the particle. The -SFR group and particle can be the same as discussed above. This type of modified particle can be prepared by heating a particle, like carbon black, with a organic group comprising a stable free radical in a solvent, such as toluene and preferably, in an inert atmosphere. With this modified particle having an attached organic group having a -SFR group, polymers can be attached onto the -SFR group by reacting the modified particle with a polymerizable monomer as discussed above using the same procedure.

With any of the above-described groups containing the -SFR group, the modified particle or aggregate containing the -SFR group or the polymerized versions thereof can be terminated by any means known to those skilled in the art in view of the present application so that a terminated moiety (-T) is located in the position of the -SFR group in the formulas above. In particular, the -SFR group can be replaced with a proton (e.g., hydrogen atom), subjected to disproportionation, or replaced with a chemical group through group transfer and the like. For instance, the -SFR group can be replaced with a metal containing group (e.g., tin or tin compound), a hydroxy group, or a halide group. For purposes of the present invention, the terminated moiety includes any chemical group capable of forming a chemical bond by substitution or replacement of the -SFR group, by one or multiple steps. For instance, the hydroxy group or halide group replacing the -SFR group can then be

subsequently modified or replaced with chemical groups, such as organic groups, by such means as conventional oxidation reactions known to those skilled in the art. This termination of removing the -SFR group and replacing it or terminating it with another group can be accomplished, for instance, by methods described in 214 ASC Nat'l Mtg, Las Vegas, September 7-11, 1997, Paper in ORGN O6l, Gravert, D.J.: Datta A.; Wentworth P., Jr.; Janda, K.D., which are incorporated in their entirety by reference herein.

The modified particles of the present invention, and preferably the polymerized and terminated versions of the modified particles of the present invention, can form part of a polymeric composition and be present with other ingredients commonly used and found in polymeric compositions.

The modified particle of the present invention can be used in a variety of applications. For instance, it can be used in coating formulations or compositions, ink formulations or compositions, or toner formulations or compositions, such as printing inks and inkjet inks, toners, automobile coatings, and the like. Also, the modified particles can be used as reinforcers for compositions, such as polymeric compositions and can also serve as impact modifiers, or as agents used to increase compatibility of a polymeric composition.

In more detail, reinforcement of elastomeric compositions including tire, hose, profile extrusion, seals, gaskets, and vibration isolation units, as well as the specific reinforcement of a single elastomer phase in a multiphase elastomer blend composition; reinforcement of thermoplastic compositions such as polyolefines, styrenic, acrylics, polyesters and polyamides, and thermoplastic

elastomers and thermoplastic polyolefines: reinforcement of thermoset compositions, *e.g.*, acrylics: impact modification of thermoplastic compositions; impact modification of thermosets: highly dispersible masterbatch for pigmentation, reinforcement, and/or UV protection of thermoplastic compositions, coatings, thermoplastic elastomers, and crosslinked compositions; as a synthetic support for solid phase organic synthesis; as a support or medium for effluent extraction processes - both organic and inorganic components: as a catalyst support; and/or as a superadsorbant for either aqueous of hydrocarbon materials, *e.g.*, use in sanitary wear, growing medium for plants.

The modified particles of the present invention can be incorporated in and form a part of elastomeric compositions. Other conventional ingredients for elastomeric compositions can also be present, such as coupling agents and the like.

Coupling agents, as used herein, include, but are not limited to, compounds that are capable of coupling fillers such as carbon black or silica to an elastomer having one functionality which will attach to the particle and another functionality which will attach to the elastomer. Coupling agents useful for coupling silica or carbon black to an elastomer, are expected to be useful with the silicon-treated carbon blacks. Useful coupling agents include, but are not limited to, silane coupling agents such as bis(3-triethoxysilylpropyl)tetrasulfane (Si-69), 3-thiocyanatopropyl-triethoxy silane (Si-264, from Degussa AG, Germany), γ-mercaptopropyl-trimethoxy silane (A189, from Union Carbide Corp., Danbury, Connecticut); zirconate coupling

agents. such as zirconium dineoalkanolatodi(3-mercapto) propionato-O (NZ 66A, from Kenrich Petrochemicals. Inc.. of Bayonne, New Jersey); titanate coupling agents: nitro coupling agents such as N.N'-bis(2-methyl-2-nitropropyl)-1,6-diaminohexane (Sumifine 1162, from Sumitomo Chemical Co., Japan); polyalkoxysiloxane (e.g. Zeruma from the Yokohama Rubber Co. Ltd., Japan) and mixtures of any of the foregoing. The coupling agents may be provided as a mixture with a suitable carrier, for example X50-S which is a mixture of Si-69 and N330 carbon black, available from Degussa AG.

The elastomeric compounds of the present invention may be prepared from the modified particles of the present invention by compounding with any elastomer including those useful for compounding a carbon black.

Any suitable elastomer may be compounded with the modified particles to provide the elastomeric compounds of the present invention. Such elastomers include, but are not limited to, homo- or co-polymers of 1,3 butadiene, styrene. isoprene, isobutylene, 2,3-dimethyl-1,3-butadiene, acrylonitrile, ethylene, and propylene Preferably, the elastomer has a glass transition temperature (Tg) as measured by differential scanning colorimetry (DSC) ranging from about -120°C to about 0°C. Examples include, but are not limited, styrene-butadiene rubber (SBR), natural rubber, polybutadiene, polyisoprene, and their oil-extended derivatives. Blends of any of the foregoing may also be used.

Among the rubbers suitable for use with the present invention are natural rubber and its derivatives, such as chlorinated rubber and epoxidized rubber. The modified particles of the present invention may also be used with

synthetic rubbers such as: copolymers of from about 10 to about 70 percent by weight of styrene and from about 90 to about 30 percent by weight of butadiene such as copolymer of 19 parts styrene and 81 parts butadiene, a copolymer of 30 parts styrene and 70 parts butadiene, a copolymer of 43 parts styrene and 57 parts butadiene and a copolymer of 50 parts styrene and 50 parts butadiene; polymers and copolymers of conjugated dienes such as polybutadiene, polyisoprene, polychloroprene, and the like, and copolymers of such conjugated dienes with an ethylenic group-containing monomer copolymerizable therewith such as styrene, methyl styrene, chloromethylstyrene, acrylonitrile, 2-vinyl-pyridine, 5-methyl 2- vinylpyridine, 5-ethyl-2-vinylpyridine, 2-methyl-5-vinylpyridine, alkyl-substituted acrylates or methacrylates, vinyl ketone, methyl isopropenyl ketone, methyl vinyl ether, alpha-methylene carboxylic acids and the esters and amides thereof such as acrylic acid, methacrylic acid, and dialkylacrylic acid amide; also suitable for use herein are copolymers of ethylene and other high alpha olefins such as propylene, butene, pentene, hexene, and octene. Other monomers that could be used include norbornene and hex-1,5-diene, and the like.

The rubber compositions of the present invention can therefore contain one or more elastomers, curing agents, reinforcing fillers, coupling agents, and, optionally, various processing aids, oil extenders, and antidegradents. In addition to the examples mentioned above, the elastomer can be, but is not limited to, polymers (e.g., homopolymers, copolymers, and terpolymers) manufactured from 1,3 butadiene, styrene, isoprene, isobutylene, 2,3-dimethyl-1,3-butadiene, acrylonitrile, ethylene, propylene, and the like. It is preferred

that these elastomers have a glass transition point (Tg), as measured by DSC, between -120°C and 0°C. Examples of such elastomers include poly(butadiene), poly(styrene-co-butadiene), and poly(isoprene).

Elastomeric compositions disclosed in the present invention include, but are not limited to, vulcanized compositions (VR), thermoplastic vulcanizates (TPV), thermoplastic elastomers (TPE) and thermoplastic polyolefins (TPO). TPV, TPE, and TPO materials are further classified by their ability to be extruded and molded several times without loss of performance characteristics.

The elastomeric compositions may include one or more curing agents such as, for example, sulfur, sulfur donors, activators, accelerators, peroxides, and other systems used to effect vulcanization of the elastomer composition.

The resultant elastomeric compounds containing the aggregates of the present invention and optionally containing one or more coupling agents may be used for various elastomeric products such as a tread compound, undertread compound, sidewall compound, wire skim compound, innerliner compound, bead, apex, any compound used in carcass and other components for vehicle tires, industrial rubber products, seals, timing belts, power transmission belting, and other rubber goods.

In an embodiment of the present invention, the elastomeric compositions of the present invention, which contain at least one modified particle of the present invention, can have a total residue after nitrogen pyrolysis at 650°C of from about 1% to about 60% by weight.

For purposes of the present invention, the ink includes at least one type of polymerized-terminated modified particle, and at least one ink vehicle. The

inkjet ink formulation includes at least one type of polymerized terminated modified particle, and at least one inkjet ink vehicle. Generally, the formulations described in WO 97/47699 with respect to coatings and inks can be used herein, however, incorporating the modified particles of the present invention. The coating formulations contain at least one type of polymerized-terminated modified particle and at least one suitable solvent. Other conventional additives may be incorporated into the coating formulations, such as a binder.

Each of these formulations can contain additional conventional colorants and other optional, conventional ingredients or additives, for instance as described in U.S. Patent Nos. 5,571,311; 5,672,198; 5,266,361; 5,707,432 such as a humectant, binders, dyes, biocides, surfactants, penetrants. All of these patents are incorporated herein in their entirety by reference herein.

The toner can contain at least one polymerized-terminated modified particle and resin particles.

The conventional and standard ingredients or additives for toner formulations, such as those described in U.S. Patent Nos. 5,278,018; 5,275,900; 5,695,899 and 5,116,712, can be used in the present invention, and are incorporated in their entirety by reference herein. The toner can be a positively or negatively charged toner composition.

In the various products incorporating the modified particles of the present invention, one or more types of other particles can also be present, such as a carbon product (e.g., carbon black), metal oxide (e.g., silica, zinc oxide, and aluminum oxide), metal silicate (e.g., clay, aluminum, calcium,

magnesium silicates), modified silica, modified carbon products having an attached organic group, an aggregate comprising at least one carbon phase and at least one silicon-containing species phase optionally having an attached organic group, carbon black at least partially coated with silica, or any combination thereof. In any product mentioned herein, more than one type of modified particle of the present invention can be present in the various products described above.

The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the invention.

EXAMPLES

Example 1

Attachment of 2,2,6,6 tetramethyl piperidinyloxy free radical (TEMPO) to carbon black.

TEMPO and carbon black grade Vulcan 7H were added to toluene and heated under an inert atmosphere at 130 °C for 96 hours. The carbon black was filtered from the toluene, washed with deionized water, and dried.

Kjeld analysis of the resultant carbon black indicated that the nitrogen content of the carbon black had increased from 0.040% to 0.57% by weight. This equates to 0.09 micromoles of TEMPO attachment per sq meter of carbon black surface area.

Comparing this example with attachment of sulfonic acid via a diazotization process, this equates to about 3% of surface coverage.

Example 2

The TEMPO modified carbon black prepared in Example 1 was combined with freshly distilled styrene and heated for various time intervals indicated in the Table under an inert argon atmosphere.

After completion of the specific time interval, the reaction was terminated by removing the heat source. The treated carbon black samples were filtered and extracted under Soxhlet refluxing conditions with tetrahydrofuran for 48 hours.

Analysis of the treated carbon black samples for organic content was carried out using TGA analysis and heating rate of 20° C/minute under a nitrogen flow rate of 50 ml/minute.

Temperature (°C)	Time (hours)	organic content (% by weight of carbon black)
125	16	1.12%
150	16	2.46%
130	72	16.5%

Example 3

Vinyl benzene functionalized carbon black prepared by the diazotization of amino styrene (using the procedure in U.S. Patent No. 5,571,311) was reacted with benzoyl peroxide and TEMPO for 16 hours at 70 °C under an argon atmosphere. The resultant carbon black was extracted with tetrahydrofuran and submitted for nitrogen analysis using the Kjeld technique,

which indicates 2 micromoles of TEMPO attachment per sq. meter of carbon black surface area.

Example 4

The modified carbon black described in Example 3 was heated with styrene under an inert argon atmosphere for 72 hours at 130 °C. The reacted carbon black was extracted with tetrahydrofuran under Soxhlet reflux conditions for 48 hours to remove any unattached polystyrene. TGA analysis indicated that the reacted carbon black contained 35% (by weight of carbon black) organic material.

Example 5 (Comparative)

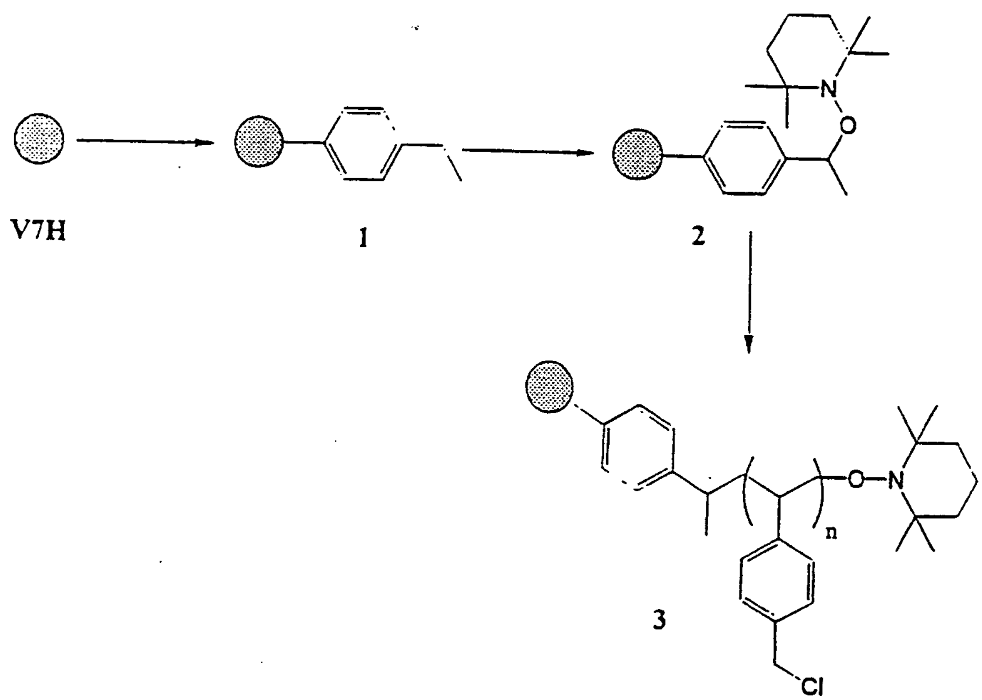
Using the procedure described by Georges in *Macromolecules*, vol. 26, pages 2987-8, (1993), a TEMPO terminated polystyrene was produced with a molecular weight, determined by GPC, of 11,200 and a polydispersity of 1.3.

Example 6 (Comparative)

The TEMPO terminated polystyrene produced in Example 5 was heated with carbon black in toluene under an inert argon atmosphere, and under the conditions set forth in the Table below. The resultant carbon black was extracted with tetrahydrofuran to remove unattached polymer, and the residual polymer attached to carbon particle was determined by TGA analysis.

Carbon Black Amount (by weight)	Polystyrene Amount (by weight)	Temperature (°C)	Time (hours)	Polymer Attachment by TGA (by weight)
10%	90%	140	44	9.4%
50%	50%	125	23	6.2%

Example 7



Ethylaniline Carbon Black Adduct 1

To a suspension of ethylaniline (4 mmol) in water (60mL) was added

hydrochloric acid (37%, 8.0 mmol) and Vulcan® 7H carbon black (10g). A solution of sodium nitrite (4.4 mmol) in water (5 mL) was added slowly and the solution stirred under air for 30 min. The temperature was increased to 70°C and stirring continued for 3.5 h. The solution was filtered and washed with water (4 x 100 mL) and dried in a vacuum oven for 24 h.

Tempo Carbon Black Adduct 2

The modified carbon black 1 (50g, 0.4 mmol/g, 20 mmol) was purged with N_2 for 30 min, followed by addition of toluene (250 mL), and TEMPO (40 mmol).. t-Butylperoxide (100 mmol) was added dropwise and the solution heated at 100°C for 48h. Methanol (100 mL) was added, and the modified carbon black removed by filtration, followed by washing with methanol into the washings were colorless (4 x 200 mL).

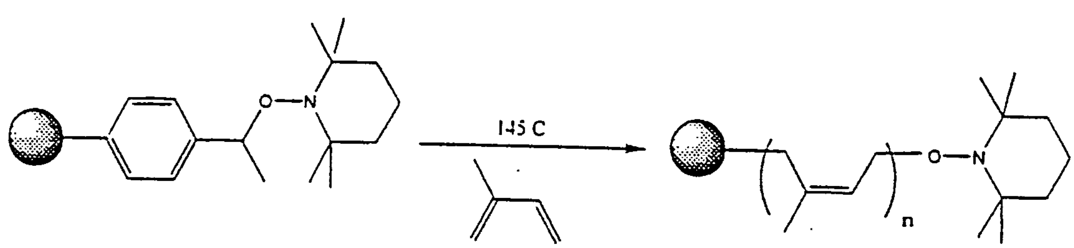
Poly(chloromethylstyrene) Modified Carbon Black 3

The modified carbon black 2 (10 g, 4 mmol) was purged with N_2 for 30 min., followed by addition of toluene (50 mL) and chloromethylstyrene (40 mmol). The solution was heated at 130°C for 72 h with stirring under nitrogen. Methanol (50 mL) was added and the solution filtered. The residue was washed with methanol until the washings were colorless (4 x 100 mL). An additional soxhlet extraction was conducted for 72h on samples intended for analysis.

While ethyl aniline was diazotized onto carbon black, this method is equally applicable to other particle surfaces where an alkyl group or other group containing an abstractable proton is available or able to be applied by chemical reaction. By-products of this reaction are limited to t-butanol and unreacted TEMPO, allowing facile purification and recycling of products and reagents. This method may be

utilized for the abstraction of a proton from an alkyl group or other group by any peroxide. The material formed may then either be employed as a initiator for "living" free radical polymerizations by addition of a monomer, or purified by precipitation and/or extraction before reacting with a monomer. Reaction of the TEMPO adduct under standard TEMPO "living free radical polymerization conditions results in the formation of a polymer, as analyzed by elemental analysis and TGA. This method may be utilized to polymerize any reactive monomer known to react under "living" free radical polymerization conditions. In addition to the cost benefits that this method provides, it also provides a cleaner route to industrial scale polymer modified particles.

Example 8



Isoprene (300mL) was added to TEMPO modified V7H (20g, 0.35 mmol/g) in a Parr pressure reactor. The reactor was sealed, degassed, and pressurized with Argon. The mixture was heated to 145°C for 18h. The resulting black suspension was precipitated into rapidly agitating methanol and isolated by filtration. The black solid was dried at 70°C.

Analysis:

48.32wt% Isoprene (TGA)

T_g (onset) = -59.25°C

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A modified particle comprising a particle having attached a group having the formula:

$$-A-R^1-\underset{\displaystyle R^3}{\overset{\displaystyle R^2}{\overset{|}{\underset{|}{C}}}}-SFR \qquad (I),$$

wherein A represents at least one aromatic group or at least one alkyl group; R^1 represents a bond, an arylene group, an alkylene group,

$$-O-,\ -NH-,\ -S-,\ -OR^4-,\ -NR^4-,\ \overset{|}{-S}=O,\ \overset{|}{-C}=O,\ \underset{\underset{|}{O}}{\underset{|}{-C}}=O,\ \underset{\underset{|}{O}}{\underset{|}{-S}}=O,$$

$$\underset{\underset{\displaystyle O}{|}}{\overset{\overset{\displaystyle O}{|}}{-P}}=O \quad \text{or,} \quad \underset{\underset{\underset{|}{O}}{|}}{\overset{\overset{\displaystyle OR^4}{|}}{-P}}=O$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein each R^5, which is the same or different, represents an alkyl group or an aryl group; and SFR represents a stable free radical.

2. The modified particle of claim 1, wherein said SFR has the formula:

$$-O-N\begin{matrix}/R^6\\ \backslash R^7\end{matrix} \qquad (V) \qquad \text{or}$$

$$-O-Ar^2 \qquad (VI)$$

wherein R^6 and R^7, which can be the same or different, represent as substituted or unsubstituted alkyl or cycloalkyl group; or R^6 and R^7 together form a cycloalkyl

group; and Ar^2 represents an aromatic group.

3. The modified particle of claim 1, wherein said particle is a carbon product, a colored pigment other than a carbon product, a metal oxide, a metal hydroxide, or mixtures thereof.

4. The modified particle of claim 1, wherein said particle is graphite, vitreous carbon, activated charcoal, carbon fiber, activated carbon, or mixtures thereof.

5. The modified particle of claim 1, wherein said particle is carbon black.

6. The modified particle of claim 1, wherein said particle is an aggregate comprising at least one silicon-containing species phase and at least one carbon phase.

7. The modified particle of claim 1, wherein said particle is an aggregate comprising at least one metal-containing species phase and at least one carbon phase.

8. The modified particle of claim 1, wherein said SFR is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

9. A modified particle or aggregate comprising a) an aggregate comprising at least one carbon phase and at least one metal-containing species phase, an aggregate comprising at least one carbon phase and at least one silicon-containing

species phase, a metal oxide, or a metal hydroxide and b) attached to said particle or aggregate, a group having the formula:

$$-\text{CoupA}\left[\begin{array}{c} R^{8} \\ | \\ C - \text{SFR} \\ | \\ R^{9} \end{array}\right]_{n} \qquad \text{(II)},$$

wherein CoupA represents a Si-based group, a Ti-based group, a Cr-based group, or a Zr-based group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NHR^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein each R^{10}, which is the same or different, represents an alkyl group or an aryl group; SFR represents a stable free radical; and n is an integer of from 1 to 3.

10. The modified particle or aggregate of claim 9, wherein said metal-containing species phase comprises an aluminum-containing species phase, a zinc-containing species phase, a magnesium-containing species phase, a calcium-containing species phase, a titanium-containing species phase, a vanadium-containing species phase, a cobalt-containing species phase, a nickel-containing species phase, a zirconium-containing species phase, a tin-coating species phase, an antimony-containing species phase, a chromium-containing species phase, a neodymium-containing species phase, a lead-containing species phase, a cesium-containing species phase, an iron-containing species phase, a molybdenum-containing species phase, or mixtures thereof.

11. The modified particle or aggregate of claim 9, wherein said SFR is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

12. The modified particle or aggregate of claim 9, wherein said particle or aggregate is an aggregate comprising a carbon phase and a metal-containing species phase or an aggregate comprising a carbon phase and silicon-containing species phase.

13. A modified particle comprising a particle having attached a group having the formula:

$$-A-R^1-\underset{R^3}{\overset{R^2}{\overset{|}{\underset{|}{C}}}}-X-SFR \qquad \text{(III)}.$$

wherein A represents at least one aromatic group or at least one alkyl group; R^1 represents a bond, an arylene group, an alkylene group,

$$-O-,\ -NH-,\ -S-,\ -OR^4-,\ -NR^4-,\ -\overset{|}{S}=O,\ -\overset{|}{C}=O,\ -\underset{\underset{|}{O}}{C}=O,\ -\underset{\underset{|}{O}}{S}=O,$$

$$-\overset{\overset{|}{O}}{\underset{\underset{O}{\|}}{P}}=O \quad \text{or,} \quad -\overset{\overset{OR^4}{|}}{\underset{\underset{|}{O}}{P}}=O$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein each R^5, which is the same or

different, represents an alkyl group or an aryl group; SFR represents a stable free radical; and X represents a polymer formed from at least one polymerizable vinyl or diene containing monomer.

14. The modified particle of claim 13, wherein said particle is a carbon product, a colored pigment other than a carbon product, a metal oxide, a metal hydroxide, or mixtures thereof.

15. The modified particle of claim 13, wherein said particle is graphite, carbon black, vitreous carbon, activated charcoal, carbon fiber, activated carbon, or mixtures thereof.

16. The modified particle of claim 13, wherein said particle is an aggregate comprising at least one silicon-containing species phase and at least one carbon phase.

17. The modified particle of claim 13, wherein said particle is an aggregate comprising at least one metal-containing species phase and at least one carbon phase.

18. The modified particle of claim 13, wherein said particle is carbon black.

19. The modified particle of claim 13, wherein said SFR is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

20. A modified particle or aggregate comprising a) an aggregate comprising at least one carbon phase and at least one metal-containing species phase, an aggregate comprising at least one carbon phase and at least one silicon-

containing species phase, a metal oxide, or a metal hydroxide and b) attached to said particle or aggregate a group having the formula:

$$-\mathrm{CoupA}\left[\begin{array}{l} \;R^8 \\ \;\,| \\ \;C\ -X-SFR \\ \;\,| \\ \;R^9 \end{array}\right]_n$$

wherein CoupA represents a Si-based group, a Ti-based group, a Cr-based group, or a Zr-based group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NH^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein each R^{10}, which is the same or different, represents an alkyl group or an aryl group: SFR represents a stable free radical: X represents a polymer formed from at least one polymerizable vinyl or diene containing monomer; and n is an integer of from 1 to 3.

21. The modified particle or aggregate of claim 20, wherein said metal-containing species phase comprises an aluminum-containing species phase, a zinc-containing species phase, a magnesium-containing species phase, a calcium-containing species phase, a titanium-containing species phase, a vanadium-containing species phase, a cobalt-containing species phase, a nickel-containing species phase, a zirconium-containing species phase, a tin-containing species phase, an antimony-containing species phase, a chromium-containing species phase, a neodymium-containing species phase, a lead-containing species phase, a tellurium-containing species phase, a barium-containing species phase, a cesium-containing

species phase, an iron-containing species phase, a molybdenum-containing species phase, or mixtures thereof.

22. The modified particle or aggregate of claim 20, wherein said particle or aggregate is an aggregate comprising at least one carbon phase and at least one metal-containing species phase or an aggregate comprising at least one carbon phase and at least one silicon-containing species phase.

23. The modified carbon-metal aggregate of claim 20, wherein said SFR is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

24. A modified particle comprising a particle having directly attached an organic group comprising a -SFR group, wherein -SFR represents a stable free radical.

25. The modified particle of claim 24, wherein said particle is a carbon product, a colored pigment other than a carbon product, a metal oxide, a metal hydroxide, an aggregate comprising at least one silicon-containing species phase and at least one carbon phase, an aggregate comprising at least one metal-containing species phase and at least one carbon phase, or mixtures thereof.

26. The modified particle of claim 24, wherein said particle is graphite, carbon black, vitreous carbon, activated charcoal, carbon fiber, activate carbon, or mixtures thereof.

27. The modified particle of claim 24, wherein said particle is carbon black.

28. The modified particle of claim 24, wherein said SFR is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

29. A modified particle comprising a particle having attached a group having the formula:

-X-SFR

wherein SFR represents a stable free radical and X, which is directly attached to said particle, represents a polymer formed from at least one polymerizable monomer.

30. The modified particle of claim 29, wherein said particle is a carbon product, a colored pigment other than a carbon product, a metal oxide, a metal hydroxide, an aggregate comprising at least one silicon-containing species phase and at least one carbon phase, an aggregate comprising at least one metal-containing species phase and at least one carbon phase, or mixtures thereof.

31. The modified particle of claim 29, wherein said particle is graphite, carbon black, vitreous carbon, activated charcoal, carbon fiber, activated carbon, or mixtures thereof.

32. The modified particle of claim 29, wherein said particle is carbon black.

33. The modified particle of claim 29, wherein said SFR is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

34. The modified particle of claim 29, wherein said polymerizable monomer is a vinyl or diene containing monomer.

35. A method for preparing the modified particle of claim 1, comprising reacting a particle having an attached vinyl or diene substituted aromatic group or alkyl group with a reactive free radical source and a stable free radical source.

36. The method of preparing the modified particle of claim 13, comprising reacting the modified particle of claim 1 with a polymerizable vinyl or diene containing monomer.

37. A method of preparing the modified particle of claim 24, comprising heating a stable free radical with a particle at a temperature above 80°C.

38. A modified particle comprising a particle having attached a group having the formula:

$$-A-R^1-\underset{R^3}{\underset{|}{\overset{R^2}{\overset{|}{C}}}}-X-T \qquad \text{(III)},$$

wherein A represents at least one aromatic group or at least one alkyl group; R^1 represents a bond, an arylene group, an alkylene group,

$$-O-,\ -NH-,\ -S-,\ -OR^4-,\ -NR^4-,\ -\overset{|}{S}=O,\ -\overset{|}{C}=O,\ -\underset{\underset{|}{\underset{O}{|}}}{C}=O,\ -\underset{\underset{|}{\underset{O}{|}}}{S}=O,$$

$$\overset{\overset{|}{\overset{O}{|}}}{\underset{\underset{O}{\|}}{-P=O}} \quad \text{or,} \quad \overset{\overset{OR^4}{|}}{\underset{\underset{|}{\underset{O}{|}}}{-P=O}}$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein each R^5, which is the same or different, represents an alkyl group or an aryl group; X represents a polymer formed from at least one polymerizable vinyl or diene containing monomer; and T represents a terminated moiety.

39. A modified particle or aggregate comprising a) an aggregate comprising at least one carbon phase and at least one metal-containing species phase, an aggregate comprising at least one carbon phase and at least one silicon-containing species phase, a metal oxide, or a metal hydroxide and b) attached to said particle or aggregate a group having the formula:

$$-\mathrm{CoupA}\left[\begin{array}{c} R^8 \\ | \\ C - X - T \\ | \\ R^9 \end{array}\right]_n$$

wherein CoupA represents a Si-based group, a Ti-based group, a Cr-based group, or a Zr-based group; R^8 and R^9, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^{10}$, $-NH^{10}$, $-NR^{10}R^{10}$, or $-SR^{10}$, wherein each R^{10}, which is the same or different, represents an alkyl group or an aryl group; X represents a polymer formed from at least one polymerizable vinyl or diene containing monomer; T is a terminated moiety and n is an integer of from 1 to 3.

40. A modified particle comprising a particle having attached a group having the formula:

-X-T

wherein X, which is directly attached to said particle. represents a polymer formed from at least one polymerizable monomer; and T represents a terminated moiety.

41. An elastomeric composition comprising at least one elastomer and the aggregate of claim 38 and optionally a coupling agent.

42. The elastomeric composition of claim 41, wherein said elastomer comprises natural rubber. polyisoprene. polybutadiene. emulsion SBR, solution SBR, functionalized SBR. NBR, butyl rubber. EPDM. EPM. or homo- or co-polymers based on or containing 1,3 butadiene. styrene. isoprene. isobutylene. 2.3-dimethyl-1,3-butadiene, acrylonitrile, ethylene. propylene, or derivatives thereof.

43. The elastomeric composition of claim 41. further comprising a crosslinking agent. reinforcing filler, a coupling agent. processing aids. oil extenders, antidegradents. or combinations thereof.

44. The elastomeric composition of claim 41. further comprising silica, carbon black, or mixtures thereof.

45. The elastomeric composition of claim 41. further comprising silica, carbon black, modified carbon black having an attached organic group, modified silica, carbon black at least partially coated with silica. an aggregate comprising at least one carbon phase and at least one silicon-containing species phase, an aggregate containing at lease one carbon phase and at least one metal-containing species phase, or combinations thereof.

46. The elastomeric compostion of claim 41, wherein said elastomeric composition has low hysteresis at high temperature, wherein said high temperature is from 20 to 100°C.

47 . A tire or compound thereof comprising the elastomeric composition of claim 41.

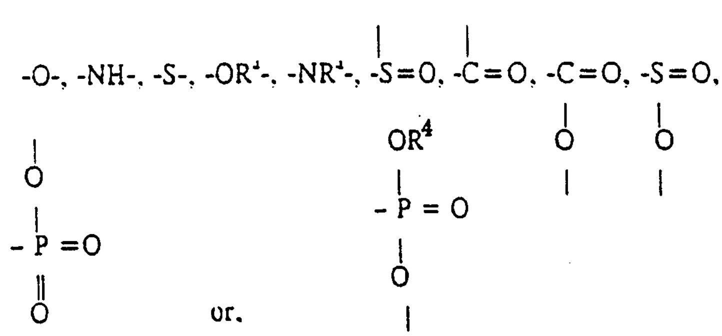
48. An article comprising at least one component made from the elastomeric composition of claim 41.

49. The article of claim 48, wherein said article is a tire component, a timing belt, or a power transmissioin belt.

50. A method of making a modified particle comprising a particle having attached a group having the formula:

$$-A-R^1-\overset{\displaystyle R^2}{\underset{\displaystyle R^3}{\overset{|}{\underset{|}{C}}}}-SFR$$

wherein A represents an aromatic group or an alkyl group; R^1 represents a bond, an arylene group, an alkylene group,



wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein each R^5, which is the same or different, represents an alkyl group or an aryl group; and SFR represents a stable free radical, wherein said method comprises reacting a) a particle having attached an aromatic group or an alkyl group with a group containing an abstractable proton and which leaves behind a carbon-centered radical when the proton is abstracted with b) a reactive free radical source and c) a stable free radical source.

51. The method of claim 1, wherein said SFR has the formula:

$$-O-N\begin{matrix} / R^6 \\ \backslash R^7 \end{matrix} \qquad \text{(V)} \qquad \text{or}$$

$$-O-Ar^2 \qquad \text{(VI)}$$

wherein R^6 and R^7, which can be the same or different, each represent a substituted or unsubstituted alkyl or cycloalkyl group; or R^6 and R^7 together forms a cycloalkyl group Ar^2 represents an aromatic group.

52. The method of claim 50, wherein said particle is a carbon product, a metal oxide, a metal hydroxide, or mixtures thereof.

53. The method of claim 50, wherein said particle is graphite, vitreous carbon, activated charcoal, carbon fiber, activated carbon, or mixtures thereof.

54. The method of claim 50, wherein said particle is carbon black.

55. The method of claim 50, wherein said particle is an aggregate comprising a silicon-containing species phase and a carbon phase.

56. The method of claim 50, wherein said particle is an aggregate comprising a metal-containing species phase and a carbon phase.

57. The method of claim 50, wherein said stable free radical source is 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, 2,2,6,6-tetramethyl-1-piperindinyloxy, or derivatives thereof.

58. The method of claim 50, wherein said reactive free radical source comprises an organic peroxide or an azo initiator.

59. The method of claim 50, wherein said reactive free radical source is a benzoyl peroxide or a t-butyl peroxide.

60. The method of claim 50, wherein said reactive free radical source comprises t-butyl peroxide.

61. The method of claim 50, wherein said group which contains an abstractable proton and is capable of leaving behind a carbon-centered radical upon proton abstraction comprises an alkyl group or an alkene group with a hydrogen atom in the alpha position to the olefinic bond.

62. The method of claim 50, wherein said group which contains an abstractable proton and is capable of leaving behind a carbon-centered radical comprises a C_1-C_{20} alkyl group.

63. The method of claim 62, wherein said C_1-C_{20} alkyl group is a methyl, ethyl, propyl, butyl, or hexyl group.

64. The method of claim 62, wherein said C_1-C_{20} alkyl group is an ethyl group.

65. The method of claim 50, wherein said aromatic group or alkyl group is first attached onto the particle and then said group containing an abstractable proton which leaves behind a carbon-centered radical upon proton abstraction is then attached onto the aromatic group or alkyl group.

66. The method of claim 50, wherein an aromatic group or alkyl group having attached thereto a group containing an abstractable proton which is capable of leaving behind a carbon-centered radical is first formed and then attached onto the particle wherein said aromatic group or alkyl group is directly attached to the particle.

67. The method of claim 50, further comprising reacting said modified particle with a polymerizable monomer to form a modified particle comprising a particle having attached a group having the formula:

$$-A-R^1-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{C}}-X-SFR \qquad \text{(III)},$$

wherein A represents an aromatic group or alkyl group; R^1 represents a bond, an arylene group, an alkylene group,

$$\text{-O-, -NH-, -S-, }-OR^4-,\ -NR^4-,\ -\overset{|}{S}=O,\ -\overset{|}{C}=O,\ -\underset{\underset{|}{\underset{O}{|}}}{C}=O,\ -\underset{\underset{|}{\underset{O}{|}}}{S}=O,$$

$$\begin{array}{c} | \\ O \\ | \\ -P=O \\ \| \\ O \end{array} \qquad \text{or,} \qquad \begin{array}{c} OR^4 \\ | \\ -P=O \\ | \\ O \\ | \end{array}$$

wherein R^4 is an alkyl or alkylene group or an aryl or arylene group; R^2 and R^3, which can be the same or different, represent hydrogen, an alkyl group, an aryl group, $-OR^5$, $-NHR^5$, $-NR^5R^5$, or $-SR^5$, wherein each R^5, which is the same or different, represents an alkyl group or an aryl group; SFR represents a stable free radical; and X represents a polymer formed from at least one polymerizable monomer.

68. The method of claim 67, wherein said polymerizable monomer is a vinyl or diene containing monomer.

69. The method of claim 67, further comprising terminating the -SFR group.

70. The method of claim 69, wherein said termination is accomplished by replacing the -SFR group with a proton, by disproportionation, or by replacement with a chemical group other than the -SFR group.

71. The method of claim 70, wherein said chemical group is a hydroxy group or halide group.

72. A toner composition comprising resin particles and the modified particles of claim 38.

73. A toner composition comprising resin particles and the modified particles of claim 39.

74. A toner composition comprising resin particles and the modified particles of claim 40.

75. An ink composition comprising an ink vehicle and the modified particles of claim 38.

76. An ink composition comprising an ink vehicle and the modified particles of claim 39.

77. An ink composition comprising an ink vehicle and the modified particles of claim 40.

78. An inkjet ink composition comprising an inkjet ink vehicle and the modified particles of claim 38.

79. An inkjet ink composition comprising an inkjet ink vehicle and the modified particles of claim 39.

80. An inkjet ink composition comprising an inkjet ink vehicle and the modified particles of claim 40.

81. A coating composition comprising a solvent and the modified particles of claim 38.

82. A coating composition comprising a solvent and the modified particles of claim 39.

83. A coating composition comprising a solvent and the modified particles of claim 40.

INTERNATIONAL SEARCH REPORT

Inte[...]ional Application No
PCT/US 98/22838

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09C1/56 C09C3/08 C09C3/10 C09C3/00 C09D7/12
C09D11/00 G03G9/09 C08J3/215

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09C C09D G03G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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Information on patent family members

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